

LA-UR-76-1723

CONF 760857--1

TITLE: CONCENTRATION OF U and Np FROM Pu and Pu
ALLOYS FOR DETERMINATION BY X-RAY FLUORESCENCE

AUTHOR(S): James M. Hansel, Jr.
Calvin J. Martell
Gilbert B. Nelson
E. Arnold Hakkila

SUBMITTED TO: Advances in X-Ray Analysis,
Proceedings of 25th Annual X-Ray Conference,
Denver, CO, August 3-6, 1976.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

By acceptance of this article for publication, the publisher recognizes the Government's (license) rights in any copyright and the Government and its authorized representatives have unrestricted right to reproduce in whole or in part said article under any copyright secured by the publisher.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the USERDA.


los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

An Affirmative Action/Equal Opportunity Employer

MASTER

86
ORDERED BY THE U.S. GOVERNMENT

CONCENTRATION OF U AND Np FROM Pu AND Pu ALLOYS FOR DETER-
MINATION BY X-RAY FLUORESCENCE

J. M. Hansel, Jr., C. J. Martell, G. B. Nelson,
and E. A. Hakkila

University of California

Los Alamos Scientific Laboratory

Los Alamos, NM 87545

ABSTRACT

Methods are presented for the determination of uranium, or uranium and neptunium, in plutonium metal and plutonium alloys. Anion exchange or a combination of anion exchange - solvent extraction is used to concentrate the elements for x-ray fluorescence analysis, depending upon the impurities present and the elements to be determined. The precision for determining between 3 and 250 μg of uranium or neptunium ranges between 30 and 2%.

INTRODUCTION

Rapid analytical procedures were required for the determination of uranium or both uranium and neptunium in plutonium metal and in various plutonium alloys. Methods exist for the determination of uranium (1,2,3) or neptunium (4) in high purity plutonium metal. The x-ray fluorescence method (1) for determining uranium is time consuming, requiring three ion exchange separations, and the spectrophotometric methods are susceptible to interference from neptunium or from any plutonium that is not removed during the separation. Likewise, the spectrophotometric method for determining neptunium suffers from interference by uranium, and uranium and neptunium cannot be measured simultaneously. X-ray fluorescence is capable of providing rapid analyses with good precision and selectivity, and the final measurement of both uranium and neptunium can tolerate some contamination by plutonium. However, a separation from the major portion of the sample is needed for good sensitivity. Anion exchange, or a combination of anion exchange and solvent extraction were chosen for these separations. Several separation schemes were developed, dependent upon the alloy composition, the elements to be determined, and the following analytical requirements:

(1) a sensitivity of 1 μg or less for measuring uranium and neptunium, (2) reproducible recoveries of uranium and neptunium, and (3) carryover of less than 10 μg of plutonium with the uranium and neptunium to eliminate plutonium spectral interference with the x-ray measurement of neptunium.

SEPARATION PROCEDURES

For the simultaneous determination of uranium and neptunium in high purity plutonium metal, a sample containing between 10 and 250 μg each of uranium and neptunium is dissolved in 5 ml of 12 M HCl . Approximately 150 mg of ascorbic acid are added to reduce the plutonium to the cationic trivalent state. Uranium and neptunium remain as anions in the hexavalent and tetravalent states, respectively, and are adsorbed on a column of Dowex 1-x₄ (50 to 100 mesh) anion exchange resin which has been conditioned with 12 M HCl . The plutonium is washed through the column with 20 ml more of 12 M HCl . The adsorbed uranium and neptunium are then eluted from the column with 20 ml of 0.01 M HCl . The eluate is evaporated to near dryness, the residue is dissolved in 0.5 ml of water, and approximately 75 mg of ascorbic acid are added. Fifteen ml of 12 M HCl are added, and a second separation and concentration for x-ray analysis is performed by passing the solution six times through a filter paper impregnated with anion exchange resin. The intensities of the $\text{L}\alpha_1$ x-rays for uranium, neptunium, and plutonium and background intensities are measured. Corrections for background and for overlapping x-ray lines are applied and the corrected intensities are compared to intensities obtained for standards prepared in the same manner as the samples. The recoveries for neptunium and uranium are only approximately 35%, but they are reproducible.

For determining only uranium in plutonium alloys the dissolved sample is evaporated to near dryness and the residue is dissolved in 5 ml of 6 M HCl . Samples containing zirconium or other elements that form cations in 6 M HCl also can be dissolved in 5 ml of 6 M HCl . Approximately 150 mg of ascorbic acid are added to reduce plutonium to the cationic trivalent state. At this acidity Zr(IV) and Pu(III) remain as cations and U(VI) remain as an anion. This solution is passed through a column containing Dowex 1-x₄ anion exchange resin which has been conditioned with 6 M HCl . The plutonium, zirconium, and other cations (including neptunium) are washed through the column with 20 ml more of 6 M HCl . The adsorbed uranium is eluted with 20 ml of 0.01 M HCl which is then evaporated to a volume of approximately 200 μl . The solution is transferred dropwise using a micropipet onto a filter paper impregnated with anion exchange resin, and the paper is dried, leaving uranium highly concentrated for x-ray analysis. Only a few micrograms of zirconium and plutonium are present and do not interfere. This method is more sensitive for determining uranium than the previously described

method because all of the uranium is collected on the filter paper. However, neptunium is not adsorbed quantitatively on anion exchange resin from 6 M HCl and cannot be determined.

Gallium, if present in amounts greater than 1 mg, interferes with the determination of uranium and must be separated before the anion exchange step. After initial dissolution of the sample and evaporation to near dryness, the residue is dissolved in 5 ml of 8 M HCl and is transferred to a separatory funnel with an additional 5 ml of 8 M HCl. Twenty ml of isopropyl ether are added to the separatory funnel which is then shaken for 2 min. More than 99% of the gallium is extracted into the ether phase; the aqueous phase, containing the uranium and plutonium, is drained into a beaker and evaporated to near dryness. The uranium is then separated from plutonium using 6 M HCl as described above, or if both uranium and neptunium are to be determined, an anion exchange separation is performed from 12 M HCl.

ANALYTICAL RESULTS AND DISCUSSION

The precision of the method for determining both uranium and neptunium was calculated from data obtained by analyzing one-gram plutonium samples containing various amounts of uranium and neptunium. Relative standard deviations for uranium (Table I) and neptunium (Table II) range between 29 and 7% for determining 3 to 120 ppm of the measured elements.

TABLE I

PRECISION OF X-RAY FLUORESCENCE MEASUREMENT OF URANIUM

(12 M HCl Ion Exchange Separation; 1-g Samples)

<u>U added,</u> <u>μg</u>	<u>No. of</u> <u>determinations</u>	<u>Standard</u> <u>deviation, μg</u>	<u>Relative Standard</u> <u>deviation, %</u>
0	9	0.7	--
4	11	0.8	20
10	10	1.5	15
20	7	2.2	11
40	9	2.9	7
100	10	10	10

TABLE II

PRECISION OF NEPTUNIUM X-RAY FLUORESCENCE

(12 M HCl Ion Exchange Separation; 1-g Samples)

<u>Np added,</u> <u>μg</u>	<u>No. of</u> <u>determinations</u>	<u>Standard</u> <u>deviation, μg</u>	<u>Relative standard</u> <u>deviation, %</u>
0	9	0.9	--
3.1	10	0.9	29
10.9	4	1.8	17
20.2	9	2.6	13
40.3	9	3.2	8
116	10	8.6	7.4

The precision for determining uranium by ion exchange separation from 6 M HCl (Table III) or by combined ion exchange - solvent extraction (Table IV) is better because of the direct pipetting of the final sample onto the ion exchange discs with nearly 100% recovery of the uranium.

TABLE III

PRECISION OF X-RAY FLUORESCENCE DETERMINATION OF URANIUM

(6 M HCl Ion Exchange Separation, 0.5-g Samples)

<u>No. of</u> <u>determinations</u>	<u>U, μg</u>	<u>Standard</u> <u>deviation, μg</u>	<u>Relative standard</u> <u>deviation, %</u>
7	0	0.2	--
8	5	0.5	10
9	17	1.0	6
10	75	4.8	6
10	100	5.2	5
7	250	15	6

TABLE IV

PRECISION OF X-RAY FLUORESCENCE DETERMINATION OF URANIUM

(Combined ion Exchange - Solvent Extraction; 0.5-g Samples)

<u>No. of</u> <u>determinations</u>	<u>U, μg</u>	<u>Standard</u> <u>deviation, μg</u>	<u>Relative standard</u> <u>deviation, %</u>
6	0	0.1	--
6	10	0.4	4
4	75	0.9	1
10	100	5.5	6
6	150	10	7

The main sources of error in this method arise from the presence of elements having high absorption coefficients for anion exchange resin in hydrochloric acid, thus competing with uranium and neptunium for the active sites on the ion exchange paper. For example both zirconium and gallium are strongly absorbed from 12 M HCl onto anion exchange papers. The interference from zirconium is eliminated by reducing the acid molarity to 6 M so that zirconium behaves as a cation. For elements such as gallium, that behave as anions at acid molarities required for adsorption of uranium, other separation schemes, such as solvent extraction, can effectively eliminate interference.

A second source of potential interference results from overlapping x-ray lines of elements that may be present in microgram amounts with the uranium and neptunium on the final filter paper. Potential interference in this category includes plutonium in the neptunium determination and neptunium in the uranium determination, as shown in Table V.

TABLE V

La_1 X-RAY WAVELENGTHS FOR URANIUM, NEPTUNIUM, AND PLUTONIUM

<u>Element</u>	<u>X-Ray</u>	<u>Wavelength, A</u>	<u>Degrees 2θ (LiF)</u>
U	La_2	0.923	26.48
	La_1	0.911	26.13
Np	La_2	0.901	25.85
	La_1	0.889	25.50
Pu	La_2	0.880	25.24
	La_1	0.869	24.92

By selecting fine collimators for the x-ray spectrograph to provide line widths at one-half maximum of $0.40^\circ 2\theta$, serious overlap is eliminated. However, a correction to the neptunium x-ray intensity of 0.034 c/s per 1 c/s of plutonium intensity is required. Also a correction of 0.029 c/s of uranium x-ray intensity is required per 1 c/s of neptunium x-ray intensity. This overlap is not serious in either case, amounting to 0.17 c/s of neptunium x-ray intensity per microgram of plutonium, and 0.14 c/s of uranium x-ray intensity per microgram of neptunium.

The accuracy of the ion exchange method from 12 M HCl for determining uranium and neptunium was tested by determining uranium and neptunium in four metal samples which also were analyzed by spectrophotometric procedures. The values for neptunium (Table VI) are in good agreement by the two methods, but values for uranium (Table VII) are significantly

higher using the spectrophotometric procedure. To test the source of this bias, three solutions were prepared and analyzed by the two procedures, and these data also are included in Tables VI and VII. Solution 1 was prepared from high purity plutonium metal (200 ppm total impurities) from which uranium and neptunium were removed by an anion exchange resin separation. Solution 2 consisted of solution 1 with 107 and 115 ppm of added uranium and neptunium, respectively, and solution 3 consisted of solution 1 with 426 ppm of added uranium, 173 ppm of added neptunium, and between 20 and 600 ppm each of aluminum, copper, chromium, iron, manganese, molybdenum, nickel, silicon, tin, vanadium, and tungsten to simulate an impure plutonium sample. Results for these analyses also are in good agreement between the two methods for determining neptunium, but recoveries for uranium are biased high on the spectrophotometric method for samples 1 and 2. The reason for the high bias is not known, but may be due to carryover of plutonium when uranium is separated from the plutonium.

TABLE VI
RESULTS OF SPECTROPHOTOMETRIC AND X-RAY FLUORESCENCE
MEASUREMENT OF Np

<u>Sample</u>	<u>Spectrophotometric</u>		<u>X-Ray Fluorescence</u>	
	<u>No. of anal.</u>	<u>Np found, ppm</u>	<u>No. of anal.</u>	<u>Np found, ppm</u>
Metal 1	2	< 15	2	7
Metal 2	2	40	2	38
Metal 3	2	39	2	37
Metal 4	2	< 15	2	6
Soln. 1	3	< 5	10	< 3
Soln. 2	5	113 ± 2	10	124 ± 19
Soln. 3	6	186 ± 5	24	202 ± 17

TABLE VII
RESULTS OF SPECTROPHOTOMETRIC AND X-RAY FLUORESCENCE
ANALYSES FOR U IN Pu

<u>Sample</u>	<u>Spectrophotometric</u>		<u>X-Ray Fluorescence</u>	
	<u>No. of anal.</u>	<u>U found, ppm</u>	<u>No. of anal.</u>	<u>U found, ppm</u>
Metal 1	2	30	2	16
Metal 2	2	36	2	15
Metal 3	2	35	2	13
Metal 4	2	24	2	17
Soln. 1	2	14	10	< 2
Soln. 2	2	144	10	100 ± 19
Soln. 3	3	440 ± 25	24	382 ± 37

SUMMARY

Uranium, or uranium and neptunium, may be determined rapidly in high purity plutonium metal or in a variety of plutonium alloys by one of several separation methods and subsequent x-ray fluorescence analysis.

Anion exchange procedures are used to concentrate the elements to be measured. Both uranium and neptunium are concentrated from plutonium using a 12 M HCl system. If only uranium is to be determined, a 6 M HCl system is used to effect a cleaner separation of uranium from plutonium, and also to separate elements such as zirconium that would interfere if the separation were performed from the higher acidity solutions. Neptunium is not recovered in 6 M HCl. Gallium can be removed by isopropyl ether extraction. The detection limits for measuring uranium and neptunium together are of the order of 3 ppm, or, for measuring only uranium, 1 ppm. One analyst can analyze six to eight samples daily for both elements.

ACKNOWLEDGEMENTS

The authors are indebted to R. B. Brooks, G. Coriz, and E. J. Hakkila for performing many of the analyses for this study, and to G. J. Waterbury for aid in manuscript review.

REFERENCES

1. J. A. Hayden "Determination of Uranium in Electro-Refined Plutonium by a Combined Ion-Exchange and X-Ray Fluorescence Technique," *Talanta*, 14, 721-729 (1967).
2. R. D. Gardner and W. H. Ashley, "The Spectrophotometric Determination of Trace Amounts of Uranium in High Purity Plutonium Metal," U. S. Atomic Energy Comm. Rept. LA-3551 (1966).
3. N. L. Koski, R. D. Gardner, and G. R. Waterbury, "Spectrophotometric Measurement of Uranium in Plutonium Oxide," U. S. Atomic Energy Comm. Rept. LA-5490 (1974).
4. R. G. Bryan and G. R. Waterbury, "The Spectrophotometric Determination of Neptunium," U. S. Atomic Energy Comm. Rept. LA-4061 (1969).